

IN THE CLAIMS:

1. (Previously Presented) A formulation comprising at least one granulate containing

- a) from 5 to 20 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,
- b) from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,
- c) from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,
- d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate;

where the phthalocyanine compound is of formula (1a)



wherein

PC is the phthalocyanine ring system;

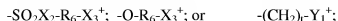
Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Zl; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;

q is 0, 1 or 2;

r is from 1 to 4;

Q₁ is a sulfo or carboxy group; or is a radical of formula

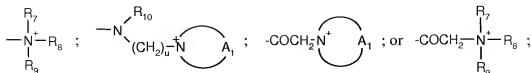


wherein

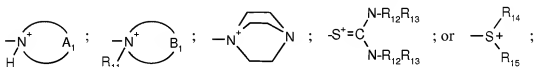
R₆ is branched or unbranched C₁-C₈alkylene; or 1,3- or 1,4-phenylene;

X₂ is -NH-; or -N-C₁-C₅alkyl-;

X_3^+ is a group of formula



and, in the case where $R_6 = C_1\text{-}C_8\text{alkylene}$, may also be a group of formula



Y_1^+ is a group of formula $\begin{array}{c} \text{---} N^+ \text{---} A_1 \\ | \\ H \end{array} ; \quad -S^+ \begin{array}{c} R_{14} \\ | \\ R_{15} \end{array} ; \text{ or } -S^+=C \begin{array}{c} N-R_{12}R_{13} \\ | \\ N-R_{12}R_{13} \end{array} ;$

t is 0 or 1;

in which above formulae,

R_7 and R_8 are each independently of the other $C_1\text{-}C_6\text{alkyl}$;

R_9 is $C_1\text{-}C_6\text{alkyl}$; $C_5\text{-}C_7\text{cycloalkyl}$; or $NR_{11}R_{12}$;

R_{10} and R_{11} are each independently of the other $C_1\text{-}C_5\text{alkyl}$;

R_{12} and R_{13} are each independently of the other hydrogen or $C_1\text{-}C_5\text{alkyl}$;

R_{14} and R_{15} are each independently of the other unsubstituted or hydroxy-, cyano-, carboxy-, $C_1\text{-}C_6\text{alkoxy-carbonyl-}$, $C_1\text{-}C_6\text{alkoxy-}$, phenyl-, naphthyl- or pyridyl-substituted $C_1\text{-}C_6\text{alkyl}$;

u is from 1 to 6;

A_1 is the balance of an aromatic 5- to 7-membered nitrogen heterocycle which may contain one or two further nitrogen atoms as ring members, and

B_1 is the balance of a saturated 5- to 7-membered nitrogen heterocycle which may contain 1 or 2 further nitrogen, oxygen and/or sulfur atoms as ring members;

A^- is an organic or inorganic anion,

and

s in the case of monovalent anions A^- is equal to r and in the case of polyvalent anions is $\leq r$, it being necessary for A_s^- to balance the positive charge; and when $r \neq 1$, the radicals Q_1 may be identical or different, and wherein the phthalocyanine ring system may also contain further solubility-imparting groups

and

where the inorganic salts are selected from the group consisting of alkali metal salts of carbonates, hydrogen carbonates, phosphates, polyphosphates, sulfates, silicates, halides and pyrophosphates,

and

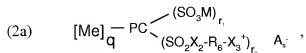
where the low-molecular weight organic acids and salts thereof are selected from the group consisting of oxalic acid, tartaric acids, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluenesulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid, polyacrylic acid and salts thereof.

2. (Original) A formulation according to claim 1, wherein the granulate comprises, as phthalocyanine compound, at least one water-soluble Zn(II), Fe(II), Ca(II), Mg(II), Na(I), K(I), Al, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III), Zr(IV), In(III), Sn(IV) or Hf(VI) phthalocyanine compound.

3. (Cancelled)

4. (Previously Presented) A formulation according to claim 1, wherein the granulate

comprises at least one phthalocyanine compound of formula



wherein

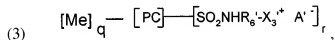
Me, q, PC, X₂, X₃ and R₆ are as defined for formula (1a),

M is hydrogen; or an alkali metal ion, ammonium ion or amine salt ion;

and the sum of the numbers r₁ and r₂ is from 1 to 4, and

A_s⁻ exactly balances the positive charge of the remainder of the molecule,

or of formula

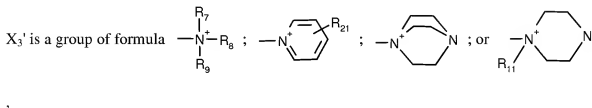


wherein

Me, q and PC are as defined for formula (1a),

R₆' is C₂-C₆alkylene;

r is a number from 1 to 4;



wherein

R₇ and R₈ are each independently of the other unsubstituted or hydroxy-, cyano-, halo- or phenyl-substituted C₁-C₄alkyl;

R₉ is R₇; cyclohexyl or amino;

R₁₁ is C₁-C₄alkyl;

R₂₁ is C₁-C₄alkyl; C₁-C₄alkoxy; halogen; carboxy; C₁-C₄alkoxy-carbonyl or hydroxy;

and

A'⁻ is a halide ion, alkylsulfate ion or arylsulfate ion;

it being possible for the radicals $-\text{SO}_2\text{NHR}'_6\text{-X}_3'^+\text{A}^-$ to be identical or different.

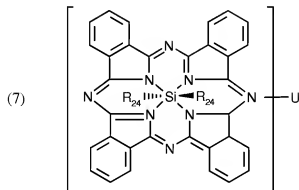
5. (Cancelled)

6. (Cancelled)

7. (Cancelled)

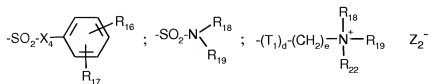
8. (Cancelled)

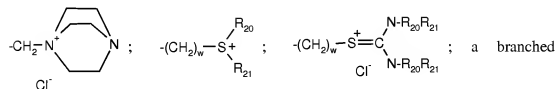
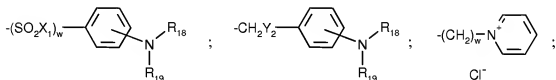
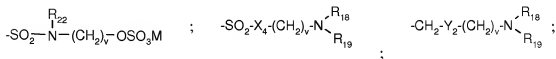
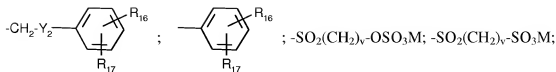
9. (Previously Presented) A formulation according to claim 1, wherein the granulate comprises at least one phthalocyanine compound of formula



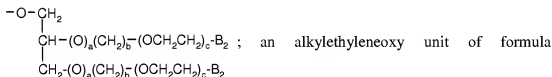
wherein

R_{24} is hydroxy; $\text{C}_1\text{-C}_{22}$ alkyl; branched $\text{C}_4\text{-C}_{22}$ alkyl; $\text{C}_1\text{-C}_{22}$ alkenyl; branched $\text{C}_4\text{-C}_{22}$ alkenyl or a mixture thereof; $\text{C}_1\text{-C}_{22}$ alkoxy; a sulfo or carboxy radical; a radical of formula





alkoxy radical of formula $\text{—O—CH} \begin{array}{c} \text{CH}_2\text{—(O)}_a\text{(CH}_2\text{)}_b\text{—(OCH}_2\text{CH}_2\text{)}_c\text{—B}_2 \\ \text{CH}_2\text{—(O)}_a\text{(CH}_2\text{)}_b\text{—(OCH}_2\text{CH}_2\text{)}_c\text{—B}_2 \end{array}$;


$$-(T_1)_d-(CH_2)_b(OCH_2CH_2)_a-B_3$$
 or an ester of formula $COOR_{23}$; and

U is $[Q_1]_r^+ A_s^-$;

$R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, B_2, B_3, M, Q_1, Q_2, A_5, T_1, X_1, X_4, Y_2, Z_2, a, b, c, d, e, r,$
 v and w therein being as defined for formulae (1a).

10. (Cancelled)

11. (Cancelled)

12. (Cancelled)

13. (Cancelled)

14. (Previously Presented) A formulation according to claim 1, wherein the granulate comprises, as anionic dispersing agent, one or more condensation products from the group consisting of: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated biphenyls or biphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkylnaphthalenesulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalenemethanesulfonates, ligno- or oxylicno-sulfonates and heterocyclic polysulfonic acids.

15. (Cancelled)

16. (Previously Presented) A formulation according to claim 1, wherein the granulate comprises, as water-soluble (but not necessarily film-forming) polymer, one or more compounds selected from the group consisting of: gelatins, polyacrylates, polymethacrylates, copolymers of ethyl acrylate, methyl methacrylate and methacrylic acid (ammonium salt), polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, copolymers of vinylpyrrolidone with long-chain olefins, poly(vinylpyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides,

copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethyl cellulose, hydroxymethyl cellulose, polyvinyl alcohols, hydrolysed and non-hydrolysed polyvinyl acetate, copolymers of maleic acid with unsaturated hydrocarbons and also mixed polymerisation products of the mentioned polymers, polyethylene glycol (MW = 4000 – 20000), copolymers of ethylene oxide with propylene oxide (MW > 3500), condensation products (block polymerisation products) of alkylene oxide, especially propylene oxide, copolymers of vinylpyrrolidone with vinyl acetate, ethylene oxide-propylene oxide addition products with diamines, especially ethylenediamine, polystyrenesulfonic acid, polyethylene-sulfonic acid, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropyl methylcellulose, sodium carboxymethyl cellulose, hydroxypropyl methylcellulose phthalate, maltodextrin, starch, sucrose, lactose, enzymatically modified and subsequently hydrated sugars, polyaspartic acid and tragacanth.

17. (Cancelled)

18. (Cancelled)

19. (Cancelled)

20. (Cancelled)

21. (Cancelled)

22. (Cancelled)

23. (Cancelled)

24. (Previously Presented) A formulation according to claim 1, wherein the granulate further comprises from 0 to 5 % by weight of a wetting agent, a disintegrant, a filler, a water-insoluble or water-soluble dye or pigment, and/or a dissolution accelerator, an optical brightener, a zeolite, talc, powdered cellulose, fibrous cellulose, microcrystalline cellulose, kaolin, TiO_2 , SiO_2 and/or magnesium trisilicate.

25. (Cancelled)

26. (Cancelled)

27. (Cancelled)

28. (Previously Presented) A formulation according to claim 1, wherein the granulate has an average particle size of $< 500 \mu\text{m}$.

29. (Cancelled)

30. (Previously Presented) A washing agent composition, washing agent additive or additive concentrate which comprises a formulation according to claim 1.

31. (Previously Presented) A composition according to claim 30, which is a component of a pre- and/or after-treatment agent, stain-removing salt, washing-power enhancer, fabric conditioner, bleaching agent and/or UV-protection enhancer.

32. (Cancelled)

33. (Previously Presented) A washing agent formulation consisting of

I) from 5 to 70 % A) of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,

II) from 5 to 60 % C) of at least one builder substance, based on the total weight of the washing agent formulation,

III) from 0 to 30 % D) of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent formulation, and

IV) from 0.001 to 1 % E) of at least one granulate as defined in claim 1, and

V) from 0 to 60 % F) of at least one further additive, and

VI) from 0 to 5 % G) water.

34. (Cancelled)

35. (Previously Presented) A process for the preparation of a granulate according to claim 1, wherein firstly an aqueous solution of the phthalocyanine compound is prepared, to which there is added the anionic dispersing agent and/or the polymer or a polymer solution, the salt and, where appropriate, further additives, and stirring is carried out until a homogeneous solution (or suspension) is obtained, and then all water, with the exception of a residual amount, is removed from the aqueous solution in a drying step, solid particles (granules) simultaneously being formed.

36. (Cancelled)

37. (Cancelled)

38. (Cancelled)

39. (Cancelled)

40. (Previously Presented) A process according to claim 35, wherein the phthalocyanine solution is purified of organic by-products by a membrane separation procedure.

41. (Previously Presented) A granulate as defined in claim 1 with the proviso that it does not contain ethoxylated stearyldiphenyloxyethyldiethyltriamine.

42. (Original) A granulate as defined in claim 41 with the proviso that it is not encapsulated and it has a substantially homogeneous distribution of ingredients.

43. (Previously Presented) A method of treating textiles which comprises contacting them with a formulation according to claim 1.

44. (Previously Presented) A formulation according to claim 1, wherein component a) comprises a mixture of zinc and aluminium phthalocyanine.

45. (Previously Presented) A formulation according to claim 1, wherein component b) comprises the condensation product of naphthalene sulfonic acid and formaldehyde.

46. (Previously Presented) A formulation according to claim 1, wherein component c) comprises alkali metal sulfates.

47. (Previously Presented) A formulation according to claim 1, wherein component c) comprises sodium sulfate.

48. (Previously Presented) A formulation according to claim 1 wherein component a) comprises a mixture of zinc and aluminium phthalocyanine, component b) comprises the condensation product of naphthalene sulfonic acid and formaldehyde and component c) comprises alkali metal sulfates.

49. (Previously Presented) A formulation according to claim 1 wherein component a) comprises a mixture of zinc and aluminium phthalocyanine, component b) comprises the condensation product of naphthalene sulfonic acid and formaldehyde and component c) comprises sodium sulphate.

50. (Previously Presented) A formulation according to claim 1 comprising at least one granulate containing

- a) from 5 to 20 % by weight based on the total weight of the granulate, of a mixture of zinc and aluminium phthalocyanine compound where Me is Zn and AlZ_4 ,
- b) from 12 to 55 % by weight based on the total weight of the granulate, of the condensation product of naphthalene sulfonic acid and formaldehyde,
- c) from 25 to 70 % by weight based on the total weight of the granulate, of alkali metal sulfates,
- d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.